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(21)Application number : 05-112947

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(54) METHOD FOR PURIFYING POLYSTYRENE BROMINATION SOLUTION

(57)Abstract:

PURPOSE: To completely and easily remove hydrogen bromide and a Friedel- Crafts catalyst from the bromination soln. to thereby obtain a brominated poly styrene excellent in heat resistance by putting the soln. into a specified amt. of water in the process for producing the brominated polystyrene by reacting polystyrene with bromine in an org. solvent in the presence of the catalyst.

CONSTITUTION: Polystyrene having a wt. average mol. wt. of 10,000-5000,000 is brominated and purified by dissolving the resin in an org. solvent, pref. a satd. aliph. halogenated hydrocarbon (e. g. methylene chloride), adding a Friedel-Crafts catalyst (e. g. aluminum chloride) to the resin soln. in an amt. of 110mol% based on the benzene ring of the resin, adding a brominating agent (e. g. bromine) in an amt. of 1-3.3mol based on 1mol of the benzene ring of the resin dropwise to the soln. to brominate the resin, putting the reaction soln. into 0.3-10 times as much water after completion of the bromination, and extracting the water layer with the solvent.

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CLAIMS

[Claim(s)]

[Claim 1] The purification approach of the polystyrene bromination reaction solution characterized by facing making a bromine react to the bottom polystyrene of existence of an Friedel Crafts reaction catalyst in an organic solvent, and manufacturing bromination polystyrene, and throwing a bromination reaction solution into underwater [twice / 0.3 - 10 weight / as many as this reaction solution].

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the purification approach of a polystyrene bromination reaction solution. Furthermore, the hydrogen bromide generated by the reaction and an Friedel Crafts reaction catalyst are removed from a polystyrene bromination reaction solution completely easily in detail, and it is related with the purification approach of a polystyrene bromination reaction solution that bromination polystyrene excellent in thermal resistance useful as a flame retarder is obtained.

[0002]

[Description of the Prior Art] Conventionally, the method of making a bromine react to the bottom polystyrene of existence of a Friedel-Crafts catalyst in an organic solvent is learned as a manufacturing method of bromination polystyrene. A hydrogen bromide is generated in this reaction. It has removed by adding the alkali water solution of the specified quantity in the reaction solution generated after the reaction, and conventionally, neutralizing in it as indicated by JP,2-215807,A. However, since the metal hydroxide generated by neutralization of an Friedel Crafts reaction catalyst is insoluble to water or an organic solvent according to this approach, it comes to mix into a product. If this metal hydroxide mixes into a product, in order to have a great bad influence on the thermal resistance of a product, the process which removes these is needed. And the filtration and liquid separation of a reaction solution of these removal are inadequate.

[0003] Removing a hydrogen bromide and a Friedel-Crafts catalyst is known by repeating several back times rinsing to which water was added to the reaction solution and deactivation of the catalyst was carried out as an approach of solving the above-mentioned technical problem. However, by this approach, in case water is added, a rapid temperature rise happens with generation of heat by deactivation of a catalyst, and the heat of dissolution to the water of the hydrogen bromide in a reaction solution, and it has a bad influence on the hue of a product. Moreover, since separation with the aqueous phase worsens, the phenomenon in which removal of a by-product becomes difficult arises. So, the product obtained is unsatisfying in quality. In addition, by this approach, in order to add water into a reaction container, it is necessary to dry a reaction container for every batch, and there is also a problem of taking a long time to obtain a product.

[0004]

[Problem(s) to be Solved by the Invention] This invention removes completely easily the hydrogen bromide generated by the reaction, and an Friedel Crafts reaction catalyst from the polystyrene bromination reaction solution which a bromine is made to react to the bottom polystyrene of existence of an Friedel Crafts reaction catalyst, and is obtained in an organic solvent, and aims at offering the purification approach of a polystyrene bromination reaction solution that bromination polystyrene excellent in thermal resistance useful as a flame retarder is obtained.

[0005] It becomes possible to carry out deactivation of the catalyst for a short time by pouring in the reaction solution generated in the container which prepared the water of the amount of specification as a result of this invention person's attaining the above-mentioned purpose and inquiring wholeheartedly. The rapid temperature rise of a reaction solution could be avoided, separation with a reaction solution and the aqueous phase became very good, the reaction container could also be used continuously, and a header and this invention were reached [that all the above-mentioned technical problems -- the bromination polystyrene which was moreover excellent in thermal resistance is obtained -- can be solved, and].

[0006]

[Means for Solving the Problem] This invention is the purification approach of the polystyrene bromination reaction solution characterized by throwing into underwater [twice / 0.3 - 10 weight / as many as this reaction solution] the

polystyrene bromination reaction solution which a bromine is made to react to the bottom polystyrene of existence of an Friedel Crafts reaction catalyst, and is obtained in an organic solvent.

[0007] As an organic solvent used for the target polystyrene bromination reaction, saturation aliphatic series halogenated hydrocarbon, such as a methylene chloride, a dichloroethane, trichloroethane, tetrachloroethane, dichloro dibromoethane, dibromoethane, tetrabromo ethane, and a carbon tetrachloride, is raised with the purification approach of this invention, for example. Not only an anhydrous solvent but when it collects so that it may usually be carried out industrially, and it contains moisture, these may carry out dehydration processing and may be the solvents of an anhydrous condition substantially. Especially in these solvents, a methylene chloride is desirable.

[0008] As a Friedel-Crafts catalyst, an aluminum chloride, the aluminium bromide, ferric chloride, iron bromide, etc. are raised, for example, and these are independent or may be used with two or more sorts of mixture. Especially an aluminum chloride is desirable also in these catalysts. since the amount of the catalyst used has the inclination for reaction time to become long if too few, and for coloring of the bromination polystyrene which will be obtained if it is made [many / too much] to become large -- 1-10 mol % of usual [per one mol of benzene rings of polystyrene] -- it is 2-6-mol % preferably.

[0009] As polystyrene, about 10,000 to 500,000 thing is usually used with weight average molecular weight, and the thing of 20,000-250,000 is desirable. Although thermal resistance becomes good in weight average molecular weight having used 10,000 or less thing so that the thermal resistance of the bromination polystyrene obtained comes to fall and weight average molecular weight becomes high, it is to about 500,000 that it can be used practical.

[0010] As for the bromine used as a brominating agent, it is desirable to use 1-3.3 mols to one mol of benzene rings of raw material polystyrene. If the bromine content of bromination polystyrene becomes inadequate and it is made [more] than 3.3 mols when fewer than one mol, residual bromines increase in number at the time of reaction termination, and it is not economical.

[0011] In order to make a bromine react to polystyrene, polystyrene is first dissolved in said aliphatic series halogenated hydrocarbon solvent completely, and a bromine is added after adding the Friedel-Crafts catalyst of the specified quantity subsequently. A bromination reaction is performed by holding preferably 0-30 degrees C of temperature at 5-20 degrees C, and dropping a bromine. There is an inclination for coloring of the bromination polystyrene from which it will be obtained if a rate of reaction becomes slow at less than 0 degree C and reaction temperature is higher than 30 degrees C to become large. It holds at further 5-15 degrees C after dropping termination, stirring is continued for 1 to 2 hours, and a reaction is completed.

[0012] If it is in this invention, after feeding into the water of the specified quantity the reaction solution obtained after reaction termination, carrying out deactivation of the catalyst and separating the aqueous phase, an organic solvent phase is washed further and an impurity is removed. The amount of water which throws in a reaction solution is 0.3 - 10 weight twice to reaction solution weight, and its 0.7 - 3 weight twice are desirable. It is not economical for a reaction solution to be heated locally, and to spoil the quality of bromination polystyrene, or for separation with the aqueous phase to come to get worse, and to make [more] it than 10 weight twice with the heat of dissolution of the hydrogen bromide whose amount of water is the catalyst and by-product which are contained in the reaction solution less than [of the amount of reaction solutions / 0.3 weight twice]. As for water temperature, it is desirable that it is 0 degree C - 30 degrees C.

[0013] In addition, when the bromine remains in the reaction solution, it is desirable to wash using the water which added the reducing agent like a sodium thiosulfate or a sodium sulfite. It is good also by the approach which may fill the saturated aliphatic hydrocarbon of lower alcohol, such as the approach of arbitration, for example, a methanol etc., or carbon numbers 5-8 with an organic solvent phase for isolating the bromination polystyrene contained in the organic solvent phase after washing, may be deposited, and distills off a solvent under the vacuum like spray drying.

[0014] Since the bromination polystyrene obtained by the approach of this invention has 1-3 bromine atoms per benzene ring and is excellent in thermal resistance, it is very useful as flame retardants of plastics, such as a polycarbonate, polyester, polypropylene, styrene resin, and a polyamide.

[0015]

[Example] An example is raised to below and it explains to it further. In addition, the section in an example and % are weight section and weight %. Carry out the dryblend of the bromination polystyrene obtained in each example and the example of a comparison in the C-3030]100 section, extrude it, and the ten sections and the antimony-trioxide [ATOX-S by NIHON SEIKO CO., LTD.] 5 section are pelletized. thermal resistance -- strengthening polyethylene-terephthalate-resin [-- Teijin, Ltd. make [] -- The test piece with a thickness of 3.2mm was fabricated for this pellet at 290 degrees C of cylinder temperatures with the injection molding machine, shaping was suspended during shaping, postforming made to pile up for 15 minutes at 290 degrees C was resumed, and b value of the test piece before and

behind stagnation was measured in color meter. It is shown that thermal resistance is so bad that b value is so large that the difference of b value before and behind stagnation is large.

[0016]

[Example 1] The methylene chloride 260 section and the polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 17 section were taught to the reaction vessel, it held at 10 degrees C, the bottom aluminum chloride of stirring 0.7 section was supplied, subsequently the bromine 55 section was dropped over 2 hours, it stirred after dropping termination for further 1 hour, and the reaction was completed. It poured into it under stirring, having reaction covered [which was obtained] it over the container which prepared the water of the 400 sections for 15 minutes, and deactivation of the catalyst was carried out. The aqueous phase was removed and the water of the 400 sections washed the organic solvent phase twice. The removed aqueous phase was transparent. The centrifugal separator separated the solid-state which trickled having applied the organic solvent phase to the methanol of the 600 sections under stirring for 3 hours, and deposited, it dried, and the bromination polystyrene (63% of bromine contents) 40.2 white section was obtained. The heat-resistant evaluation result was shown in Table 1.

[0017]

[Example 2] The methylene chloride 260 section and the polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 17 section were taught to the reaction vessel, it held at 10 degrees C, the bottom aluminum chloride of stirring 0.7 section was supplied, subsequently the bromine 66 section was dropped over 2 hours, it stirred after dropping termination for further 1 hour, and the reaction was completed. It poured into it under stirring, having reaction covered [which was obtained] it over the container which prepared the water of the 400 sections for 15 minutes, and deactivation of the catalyst was carried out. The aqueous phase was removed and the water of the 400 sections washed the organic solvent phase twice. The removed aqueous phase was transparent. The centrifugal separator separated the solid-state which trickled having applied the organic solvent phase to the methanol of the 600 sections under stirring for 3 hours, and deposited, it dried, and the bromination polystyrene (66% of bromine contents) 48.7 white section was obtained. The heat-resistant evaluation result was shown in Table 1.

[0018]

[Example 3] The bromination polystyrene (63% of bromine contents) 38.9 white section was obtained like the example 1 except making into the 1000 sections amount of water taught to a container.

[0019]

[The example 1 of a comparison] The methylene chloride 260 section and the polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 17 section were taught to the reaction vessel, it held at 10 degrees C, the bottom aluminum chloride of stirring 0.7 section was supplied, subsequently the bromine 55 section was dropped over 2 hours, it stirred after dropping termination for further 1 hour, and the reaction was completed. In addition, deactivation of the catalyst was carried out to it, having poured the water of the 50 sections on the obtained reaction solution for 90 minutes. The aqueous phase was removed and sequential washing of the organic solvent phase was carried out once 3 times in the water 200 section by the sodium-hydroxide water-solution 200 section 10%. The removed aqueous phase was white translucence. It was dropped having applied the organic solvent phase to the methanol of the 600 sections under stirring for 3 hours, the centrifugal separator separated the depositing solid-state, it dried, and the bromination polystyrene (62% of bromine contents) 39.1 white section was obtained. The heat-resistant evaluation result was shown in Table 1.

[0020]

[The example 2 of a comparison] The methylene chloride 260 section and the polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 17 section were taught to the reaction vessel, it held at 10 degrees C, the bottom aluminum chloride of stirring 0.7 section was supplied, subsequently the bromine 55 section was dropped over 2 hours, it stirred after dropping termination for further 1 hour, and the reaction was completed. It was dropped at it, having applied [water 50] it to the obtained reaction solution for 15 minutes, and deactivation of the catalyst was carried out. The aqueous phase was removed and the water of the 400 sections washed the organic solvent phase 3 times. The removed aqueous phase is white translucence and existence of an interlayer was accepted. It applied for 3 hours to the bottom of stirring to the methanol of the 600 sections of an organic solvent phase, and was dropped, the centrifugal separator separated the depositing solid-state, it dried, and the bromination polystyrene (62% of bromine contents) 39.6 white section was obtained. The heat-resistant evaluation result was shown in Table 1.

[0021]

[The example 3 of a comparison] The methylene chloride 260 section and the polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 17 section were taught to the reaction vessel, it

held at 10 degrees C, and the bottom aluminum chloride of stirring 0.7 section was supplied. Subsequently, the bromine 66 section was dropped over 2 hours, it stirred after dropping termination for further 1 hour, and the reaction was completed. It poured into it under stirring, having reaction covered [which was obtained] it over the container which prepared the water of the 80 sections for 15 minutes, and deactivation of the catalyst was carried out. The aqueous phase was removed and the water of the 200 sections washed the organic solvent phase 5 times. The removed aqueous phase was transparent. The centrifugal separator separated the solid-state which trickled having applied the organic solvent phase to the methanol of the 600 sections under stirring for 3 hours, and deposited, it dried, and the bromination polystyrene (66% of bromine contents) 47.8 yellow section was obtained. The heat-resistant evaluation result was shown in Table 1.

[0022]

[Table 1]

	耐 熱 性	
	滯 留 前 (b 値)	滯 留 後 (b 値)
実施例 1	8. 5	10. 2
実施例 2	9. 2	12. 9
実施例 3	8. 8	11. 0
比較例 1	15. 7	22. 3
比較例 2	11. 7	18. 3
比較例 3	12. 3	19. 5

[0023]

[Effect of the Invention] The effectiveness that become possible to carry out deactivation of the reaction catalyst for a short time according to the approach of this invention, and can avoid the rapid temperature rise of a reaction solution, and separation with a reaction solution and the aqueous phase becomes very good, can use a reaction container continuously, bromination polystyrene useful as a flame retarder which was moreover excellent in thermal resistance is obtained, and this invention does so is exceptional.

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behind stagnation was measured in color meter. It is shown that thermal resistance is so bad that b value is so large that the difference of b value before and behind stagnation is large.

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[0022]

[Table 1]

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実施例 1	8. 5	1 0. 2
実施例 2	9. 2	1 2. 9
実施例 3	8. 8	1 1. 0
比較例 1	1 5. 7	2 2. 3
比較例 2	1 1. 7	1 8. 3
比較例 3	1 2. 3	1 9. 5

[0023]

[Effect of the Invention] The effectiveness that become possible to carry out deactivation of the reaction catalyst for a short time according to the approach of this invention, and can avoid the rapid temperature rise of a reaction solution, and separation with a reaction solution and the aqueous phase becomes very good, can use a reaction container continuously, bromination polystyrene useful as a flame retarder which was moreover excellent in thermal resistance is obtained, and this invention does so is exceptional.

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最終頁に続く

(54) 【発明の名称】 ポリスチレン臭素化反応溶液の精製方法

(57) 【要約】

【目的】 有機溶媒中でフリーデルクラフツ反応触媒の存在下ポリスチレンに臭素を反応させて得られるポリスチレン臭素化反応溶液から、反応によって発生する臭化水素及びフリーデルクラフツ反応触媒を完全に且つ容易に除去し、難燃剤として有用な耐熱性に優れた臭素化ポリスチレンが得られるポリスチレン臭素化反応溶液の精製方法を提供する。

【構成】 有機溶媒中でフリーデルクラフツ反応触媒の存在下ポリスチレンに臭素を反応させて臭素化ポリスチレンを製造するに際し、臭素化反応溶液を該反応溶液の0.3～10重量倍の水中に投入することを特徴とするポリスチレン臭素化反応溶液の精製方法。

(2)

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【特許請求の範囲】

【請求項1】 有機溶媒中でフリーデルクラフツ反応触媒の存在下ポリスチレンに臭素を反応させて臭素化ポリスチレンを製造するに際し、臭素化反応溶液を該反応溶液の0.3～10重量倍の水中に投入することを特徴とするポリスチレン臭素化反応溶液の精製方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明はポリスチレン臭素化反応溶液の精製方法に関する。更に詳しくは、ポリスチレン臭素化反応溶液から、反応によって発生する臭化水素及びフリーデルクラフツ反応触媒を完全に且つ容易に除去し、難燃剤として有用な耐熱性に優れた臭素化ポリスチレンが得られるポリスチレン臭素化反応溶液の精製方法に関する。

【0002】

【従来の技術】従来、臭素化ポリスチレンの製造法として、有機溶媒中でフリーデルクラフツ触媒の存在下ポリスチレンに臭素を反応させる方法が知られている。この反応においては臭化水素が発生する。従来は、例えば特開平2-215807号公報に記載されているように、反応後生成した反応溶液に所定量のアルカリ水溶液を添加して中和することによって除去してきた。しかしながら、この方法によるとフリーデルクラフツ反応触媒の中和によって生成する金属水酸化物が水や有機溶媒に不溶であるため製品中に混入するようになる。かかる金属水酸化物が製品中に混入すると製品の耐熱性に多大な悪影響を及ぼすためこれらを除去する工程が必要になる。しかもこれらの除去は反応溶液の濾過や分液等では不十分である。

【0003】上記の課題を解決する方法として、反応溶液に水を加えて触媒を失活させた後数回水洗を繰返すことによって臭化水素及びフリーデルクラフツ触媒を除去することが知られている。しかしながら、この方法では水を加える際に触媒の失活による発熱と反応溶液中の臭化水素の水への溶解熱とで急激な温度上昇が起こり、製品の色相に悪影響を及ぼす。また、水相との分離が悪くなるため、副生物の除去が困難となるという現象が生じる。それ故得られる製品は品質的に満足できるものではない。加えてこの方法では反応容器中に水を加えるため、反応容器を一バッチ毎に乾燥させる必要があり、製品を得るのに長時間を要するという問題もある。

【0004】

【発明が解決しようとする課題】本発明は、有機溶媒中でフリーデルクラフツ反応触媒の存在下ポリスチレンに臭素を反応させて得られるポリスチレン臭素化反応溶液から、反応によって発生する臭化水素及びフリーデルクラフツ反応触媒を完全に且つ容易に除去し、難燃剤とし

を目的とする。

【0005】本発明者は上記目的を達成せんとして鋭意検討した結果、特定量の水を仕込んだ容器中に生成した反応溶液を注ぎ込むことによって短時間で触媒を失活させることが可能になり、反応溶液の急激な温度上昇が回避でき、反応溶液と水相との分離が非常に良好になり、反応容器も連続して使用でき、しかも耐熱性に優れた臭素化ポリスチレンが得られる等上記課題全てを解決し得ることを見出し、本発明に到達した。

10. 【0006】

【課題を解決するための手段】本発明は、有機溶媒中でフリーデルクラフツ反応触媒の存在下ポリスチレンに臭素を反応させて得られるポリスチレン臭素化反応溶液を、該反応溶液の0.3～10重量倍の水中に投入することを特徴とするポリスチレン臭素化反応溶液の精製方法である。

【0007】本発明の精製方法で対象とするポリスチレン臭素化反応に使用する有機溶媒としては、例えば塩化メチレン、ジクロロエタン、トリクロロエタン、テトラクロロエタン、ジクロロジプロモエタン、ジプロモエタン、テトラプロモエタン、四塩化炭素等の飽和脂肪族ハロゲン化炭化水素があげられる。これらは無水の溶媒だけでなく、工業的に通商行われるように回収し、水分を含有する場合は脱水処理して実質的に無水状態の溶媒であってもよい。これらの溶媒のなかでは塩化メチレンが特に好ましい。

【0008】フリーデルクラフツ触媒としては、例えば塩化アルミニウム、臭化アルミニウム、塩化鉄、臭化鉄等があげられ、これらは単独で又は二種以上の混合物で使用してもよい。これらの触媒のなかでも塩化アルミニウムが特に好ましい。触媒の使用量はあまりに少ないと反応時間が長くなり、あまりに多くすると得られる臭素化ポリスチレンの着色が大きくなる傾向があるので、ポリスチレンのベンゼン環1モル当たり通常1～10モル%、好ましくは2～6モル%である。

【0009】ポリスチレンとしては、通常重量平均分子量で10,000～500,000程度のものが使用され、20,000～250,000のものが好ましい。重量平均分子量が10,000以下のものを使用したのでは得られる臭素化ポリスチレンの耐熱性が低下するようになり、重量平均分子量が高くなるほど耐熱性はよくなるが、実用的に使用できるのは500,000程度までである。

【0010】臭素化剤として使用する臭素は原料ポリスチレンのベンゼン環1モルに対し、1～3.3モル使用するのが好ましい。1モルよりも少ない場合は臭素化ポリスチレンの臭素含有量が不十分になり、3.3モルより多くすると反応終了時に残余の臭素が多くなり、経済

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ず前記脂肪族ハロゲン化炭化水素溶媒にポリスチレンを完全に溶解し、次いで所定量のフリーデルクラフツ触媒を加えた後臭素を添加する。臭素化反応は温度を0～30℃、好ましくは5～20℃に保持して臭素を滴下することによって行う。反応温度が0℃未満では反応速度が遅くなり、30℃より高いと得られる臭素化ポリスチレンの若色が大きくなる傾向がある。滴下終了後更に5～15℃に保持して1～2時間攪拌を継続し反応を完結させる。

【0012】本発明にあつては、反応終了後得られる反応溶液を、所定量の水に投入して触媒を失活させ、水相を分離した後更に有機溶媒相を洗浄して不純物を除去する。反応溶液を投入する水量は反応溶液重量に対して0.3～10重量倍であり、0.7～3重量倍が好ましい。水量が反応溶液量の0.3重量倍未満では反応溶液中に含まれている触媒及び副生物である臭化水素の溶解熱によって反応溶液が局部的に加熱され、臭素化ポリスチレンの品質を損ねたり、水相との分離が悪化するようになり、10重量倍より多くするのは経済的ではない。水温は0℃～30℃であるのが好ましい。

【0013】なお、反応溶液に臭素が残存している場合には、例えばチオ硫酸ナトリウムや亜硫酸ナトリウムの如き還元剤を添加した水を用いて洗浄することが好ましい。洗浄後の有機溶媒相に含まれる臭素化ポリスチレンを単離するには任意の方法、例えばメタノール等の低級アルコール類又は炭素数5～8の飽和脂肪族炭化水素に有機溶媒相を注ぎ析出させてもよいし、スプレー乾燥の如き真空下で溶媒を留去する方法によってもよい。

【0014】本発明の方法で得られる臭素化ポリスチレンは、ベンゼン環1個当たり1～3個の臭素原子を有し、耐熱性に優れているので例えばポリカーボネート、ポリエステル、ポリプロピレン、スチレン系樹脂、ポリアミド等のプラスチックの難燃剤として極めて有用なものである。

【0015】

【実施例】以下に実施例をあげて更に説明する。なお、実施例中の部及び％は重量部及び重量％であり、耐熱性は強化ポリエチレンテレフタレート樹脂〔帝人（株）製C-3030〕100部に各実施例及び比較例で得た臭素化ポリスチレンを10部及び三酸化アンチモン〔日本精鉱（株）製ATOX-S〕5部をドライブレンドして押出してペレット化し、このペレットを射出成形機によりシリンダー温度290℃で厚さ3.2mmの試験片を成形し、成形中成形を一旦停止し、290℃で15分間滞留させた後成形を再開し、滞留前後の試験片のb値をカラーメーターで測定した。滞留前後のb値の差が大きい程、またb値が大きい程耐熱性が悪いことを示す。

【0016】

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重平均分子量55,000〕17部を仕込み、10℃に保持して攪拌下塩化アルミニウム0.7部を投入し、次いで臭素5.5部を2時間かけて滴下し、滴下終了後更に1時間攪拌して反応を完結させた。得られた反応溶液を、400部の水を仕込んだ容器に攪拌下15分かけて注入して触媒を失活させた。水相を除去し、有機溶媒相を400部の水で2回洗浄した。除去した水相は透明であった。有機溶媒相を600部のメタノールに攪拌下3時間かけて滴下して析出した固体を遠心分離機によって分離し、乾燥して白色の臭素化ポリスチレン（臭素含有量63％）40.2部を得た。その耐熱性の評価結果を表1に示した。

【0017】

【実施例2】反応釜に塩化メチレン260部及びポリスチレン〔大日本インキ（株）製エラストレン200、重平均分子量55,000〕17部を仕込み、10℃に保持して攪拌下塩化アルミニウム0.7部を投入し、次いで臭素6.6部を2時間かけて滴下し、滴下終了後更に1時間攪拌して反応を完結させた。得られた反応溶液を、400部の水を仕込んだ容器に攪拌下15分かけて注入して触媒を失活させた。水相を除去し、有機溶媒相を400部の水で2回洗浄した。除去した水相は透明であった。有機溶媒相を600部のメタノールに攪拌下3時間かけて滴下して析出した固体を遠心分離機によって分離し、乾燥して白色の臭素化ポリスチレン（臭素含有量66％）48.7部を得た。その耐熱性の評価結果を表1に示した。

【0018】

【実施例3】容器に仕込む水量を1000部にする以外は実施例1と同様にして白色の臭素化ポリスチレン（臭素含有量63％）38.9部を得た。

【0019】

【比較例1】反応釜に塩化メチレン260部及びポリスチレン〔大日本インキ（株）製エラストレン200、重平均分子量55,000〕17部を仕込み、10℃に保持して攪拌下塩化アルミニウム0.7部を投入し、次いで臭素5.5部を2時間かけて滴下し、滴下終了後更に1時間攪拌して反応を完結させた。得られた反応溶液に50部の水を90分かけて加えて触媒を失活させた。水相を除去し、有機溶媒相を10％水酸化ナトリウム水溶液200部で1回、水200部で3回順次洗浄した。除去した水相は白色半透明であった。有機溶媒相を600部のメタノールに攪拌下3時間かけて滴下し、析出した固体を遠心分離機によって分離し、乾燥して白色の臭素化ポリスチレン（臭素含有量62％）39.1部を得た。その耐熱性の評価結果を表1に示した。

【0020】

【比較例2】反応釜に塩化メチレン260部及びポリス

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保持して攪拌下塩化アルミニウム0.7部を投入し、次いで臭素5.5部を2時間かけて滴下し、滴下終了後更に1時間攪拌して反応を完結させた。得られた反応溶液に水50部を15分かけて滴下して触媒を失活させた。水相を除去し、有機溶媒相を400部の水で3回洗浄した。除去した水相は白色半透明であり、中間層の存在が認められた。有機溶媒相を600部のメタノールに攪拌下に3時間かけて滴下し、析出した固体を遠心分離機によって分離し、乾燥して白色の臭素化ポリスチレン（臭素含有量62%）39.6部を得た。その耐熱性の評価結果を表1に示した。

【0021】

【比較例3】反応釜に塩化メチレン260部及びポリスチレン〔大日本インキ（株）製エラストレン200、重畳平均分子量55,000〕17部を仕込み、10℃に保持して攪拌下塩化アルミニウム0.7部を投入した。次いで臭素6.6部を2時間かけて滴下し、滴下終了後更に1時間攪拌して反応を完結させた。得られた反応溶液を、80部の水を仕込んだ容器に攪拌下15分かけて注入して触媒を失活させた。水相を除去し、有機溶媒相を200部の水で5回洗浄した。除去した水相は透明であった。有機溶媒相を600部のメタノールに攪拌下3時間かけて滴下して析出した固体を遠心分離機によって分*

*離し、乾燥して黄色の臭素化ポリスチレン（臭素含有量66%）47.8部を得た。その耐熱性の評価結果を表1に示した。

【0022】

【表1】

	耐熱性	
	滞留前 (b値)	滞留後 (b値)
実施例1	8.5	10.2
実施例2	9.2	12.9
実施例3	8.8	11.0
比較例1	15.7	22.3
比較例2	11.7	18.3
比較例3	12.3	19.5

【0023】

【発明の効果】本発明の方法によれば、短時間で反応触媒を失活させることが可能になり、反応溶液の急激な温度上昇が回避でき、反応溶液と水相との分離が非常に良好になり、反応容器を連続して使用でき、しかも耐熱性に優れた難燃剤として有用な臭素化ポリスチレンが得られ、本発明の奏する効果は格別なものである。

フロンページの続き

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